Liquid Crystal Fluctuations Probed with Dynamic Soft X-ray Scattering

A.C. Price[1], L.B. Sorensen[1], and S.D. Kevan[2]
[1]Physics Department, University of Washington, Seattle, WA. 98195, USA
[2]Physics Department, University of Oregon, Eugene, OR. 97403, USA

INTRODUCTION

Robert Brown discovered the thermally driven motion of small particles in solution in 1828, and Albert Einstein provided a theoretical understanding of Brownian motion in 1905. The transverse coherence of lasers now allows us to measure reliably the Brownian motion of small particles in considerable detail, using dynamic laser light scattering. However, there are also interesting thermally driven motions of individual molecules and molecular fragments that are crucial to chemical reaction rates, catalysis, and biological function. How can we measure the molecular-scale motions of collective fluctuating systems? We cannot use laser-light scattering directly because the spatial resolution is set by the wavelength of the light, and the wavelength of visible light is much greater than the size of the molecules. However, to probe atomic- or molecular-length scales, we can in principle do the exact analogue of dynamic laser light scattering using hard or soft x-rays, assuming that sufficient coherent power is available. We report here on our initial efforts along these lines at the ALS.[1]

Hard x-rays (at wavelengths near 1 Å) have recently been used to probe relatively slow (tenths of a second to hours) atomic motion.[2-5] The measurement of fast (microsecond) molecular motion, however, requires more coherent photons than can be obtained at third-generation hard x-ray synchrotron sources. The available coherent flux of and hard or soft x-ray undulator is proportional to λ^2. Given that the brightness of hard and soft x-ray undulators is comparable, one can in principle get 2000 times more coherent photons using 44 Å soft x rays than from using 1 Å hard x-rays. The longer soft x-ray wavelengths can provide adequate spatial resolution to probe the molecular as opposed to the atomic length scale.

We have developed dynamic soft x-ray scattering and applied it to a relatively simple problem: measuring the layer fluctuations of freely suspended liquid-crystal films. We were able to achieve the same time resolution as with conventional laser-light scattering (about 1 microsecond) and 100 times better spatial resolution (44 vs. 6360 Å).

APPARATUS AND EXPERIMENTAL TECHNIQUE

A schematic of the scattering apparatus is shown in Fig. 1. Light from the 5 cm period undulator passes through the BL7 spherical grating monochromator, providing a beam with a resolving power of $E/\Delta E \sim 10^4$ and a coherent fraction $\sim 10^{-4}$. Light exiting the monochromator is spatially filtered using a two-pinhole spatial filter that selects one transverse mode. At a wavelength of ~4 nm, we achieve a coherent flux as high as 2×10^9/sec, though this was reduced in later experiments due to the introduction of a multilayer mirror upstream of the spatial filter. This light is then Bragg-scattered off a free-standing liquid crystal film that had been prepared *in situ*. Light scattered off the sample and through a pinhole (I_1) is detected with a scintillator/phototube combination. The transmitted beam was also collected with a similar detector, and this provided a reference signal, I_o.

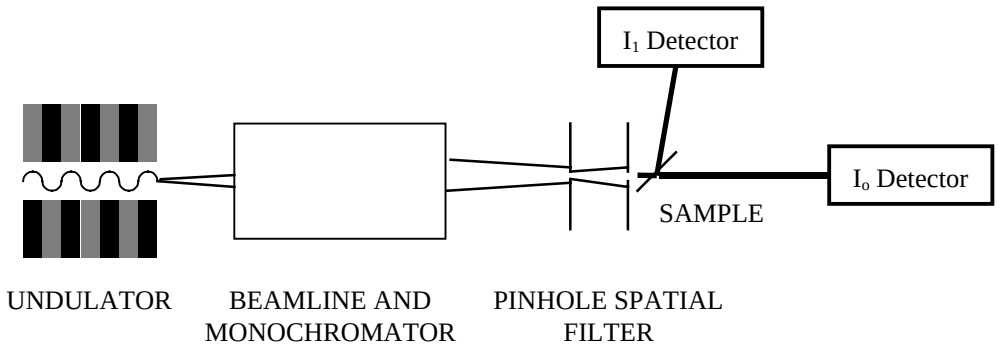

Figure 1: Schematic of the scattering apparatus, including the 8 cm undulator, the BL12 VLS monochromator, the spatial filter, the sample and CCD detector.

EXPERIMENTAL RESULTS

The liquid-crystal films used in this experiment were heated into the smectic-A phase. In the smectic-A phase, the molecules organize into layers, and these layers of the crystal can "slide" back and forth easily relative to each other. Within a layer, the molecules are free to move in liquid-like fashion. If the incident beam is spatially coherent, the intensity of photons reflected will also fluctuate because of the thermally driven motions within the sample. Such fluctuations are normally measured in terms of a normalized intensity-intensity autocorrelation function. In our experiment, forming the ratio of the autocorrelation functions of the scattered to the transmitted photons allows us partially to normalize the correlated noise in the synchrotron beam. An example of such a ratio is shown in Fig. 2.

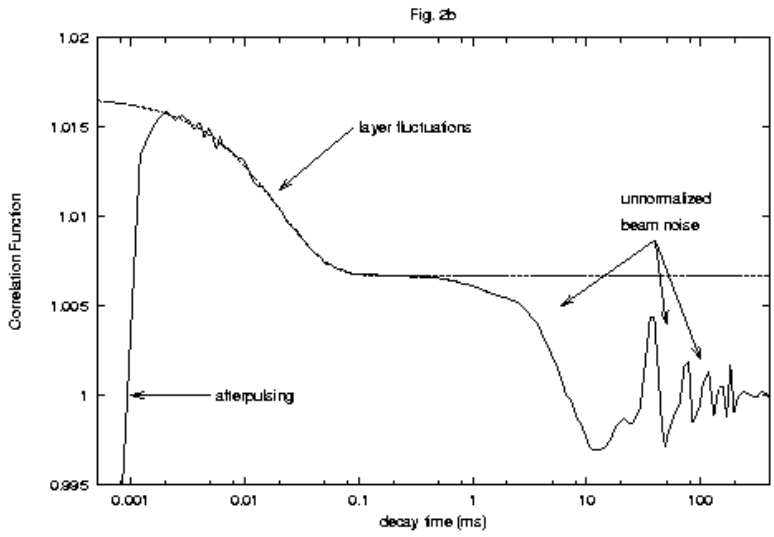

Figure 2: Normalized intensity autocorrelation function of 44 Å x-rays Bragg scattered from a free-standing smectic liquid crystal film, 4O.8. The layer fluctuations are reflected by the hump for delay times less than 50 μs.

By fitting such normalized functions to decaying exponential curves as shown in the figure, we determined the characteristic decay time of the layer fluctuations for a given film thickness. A

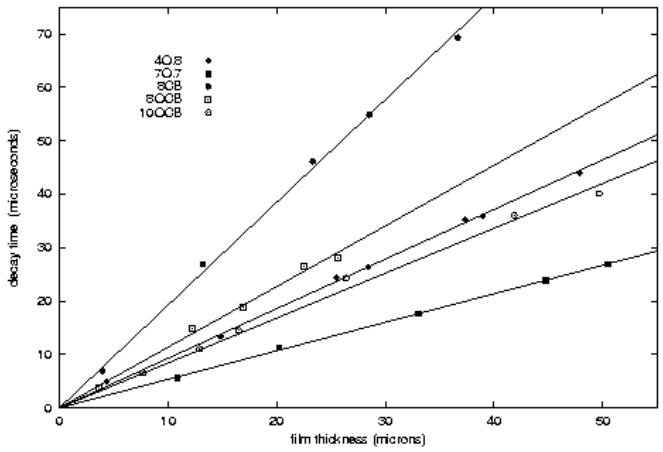

Figure 3: Characteristic decay time of the intensity autocorrelation function of light Bragg-scattered from five different free-standing smectic-A liquid crystal films as a function of film thickness.

plot of decay time vs. film thickness for the five crystal types studied shown in Fig. 3 exhibits an obvious linear relationship between delay time and film thickness. This linearity is in excellent agreement with the predictions of theoretical models and simple simulations.[6] The product of the film thickness and the layer sliding viscosity divided by twice the surface tension gives the slope of each line. The fluctuations are thus related to 'drumhead modes' wherein the entire film fluctuates without compression of the layers. To probe the layer fluctuations will require off-Bragg scattering where presently we cannot operate due to insufficient signal. With future access to the raw undulator beam on Beamline 9.0.1 (unfiltered by a monochromator and not subject to losses from optical components), the available coherent flux will increase by 1000. In this case, we should have enough signal to measure the layer fluctuations themselves.

ACKNOWLEDGMENTS

Thanks to Andrej Poniewierski, Robert Holyst, and John Toner for theoretical input concerning this experiment.

REFERENCES

1. A.C. Price, *et. al*., Phys. Rev. Lett. **82**, 755 (1999).
2. S. B. Dierker, *et al*., Phys. Rev. Lett. **75**, 449 (1995);
3. T. Thurn-Albrecht, *et al*., Phys. Rev. Lett. **77**, 5437 (1996).
4. S. G. J. Mochrie, *et al*.,Phys. Rev. Lett. **78**, 1275 (1997).
5. S. Brauer, *et al*., Phys. Rev. Lett. **74**, 2010 (1995).
6. A. Poniewierski, *et. al*., Phys. Rev. E **58**, 2027-2040 (1998).

This work was supported by the Department of Energy, Office of Basic Energy Sciences, Materials Science Division under grant number DE-FG06-86ER45275 American Chemical Society Petroleum Research Fund; University of Washington Molecular Biophysics Training Grant.

Principal Investigator: Larry Sorensen, Physics Department, University of Washington, Seattle, WA. 98195. Email: sorensen@uwaphy.phys.washington.edu. Telephone: 206-543-0360.